Measurement of Diesel Solid Nanoparticle Emissions

HEEJUNG JUNG[1], Kent Johnson[1], Tom Durbin[1], Shaohua Hu[2], David Cocker[1], Zhihua Liu [1,4] Zhongqing Zheng[1], Ajay Chaudhary [2], Tao Huai[2], Jorn Herner[2], William Robertson[2], Alberto Ayala[2] and David Kittelson[3]

[1]University of California, College of Engineering, Center for Environmental Research and Technology (CE-CERT), Riverside, CA 92521

[2]California Air Resources Board (CARB), 1001 I Street, Sacramento, CA 95814

[3]University of Minnesota, Department of Mechanical Engineering, 111 Church St. SE, Minneapolis, MN55455

[4]Beijing Institute of Technology, China

UNIVERSITY of CALIFORNIA Riverside

California Environmental Protection Agency Air Resources Board

CE-CERT Bourns College of Engineering Center for Environmental Research and Technology

UNIVERSITY OF MINNESOTA Driven to Discover℠

Introduction

The current gravimetric methods used for the legal determination of emissions have difficulty accurately quantifying Particulate Matter (PM) mass emissions as regulations continue to get more stringent. Although the US EPA issued an improved protocol for the current gravimetric method, the accuracy will continue to be an issue at a very low level emission from new vehicles. The European Particle Measurement Programme (PMP) is a particle measurement protocol which aims to measure solid particle number emissions. The PMP protocol specifies to measure particles larger than 23 nm assuming contribution of sub 23 nm solid particles are insignificant. It is a promising method to possibly complement regulatory mass measurements. The PMP protocol is included in Euro 5/6 proposed emission regulations. The proposed number emission limit of 5×10^{11} particles/km would be applicable to all categories of light-duty diesel vehicles at the Euro 5 and Euro 6 stages.

The potential of PMP protocol for heavy-duty vehicles/ engines has been recently studied in Europe and the U.S.. During CARB's previous studies on PMP they found important issues. They found there are significant number of appear-to-be solid sub-23nm particles that can make it past the PMP volatile particle remover [1]. It is very important to find out whether these operationally determined solid particles are real solid particles (such as partially burned soot or ash) less than 23nm or low-volatile compounds and to compare particle emissions during cycles and real world on-road driving as either case will suggest modification of the PMP method.

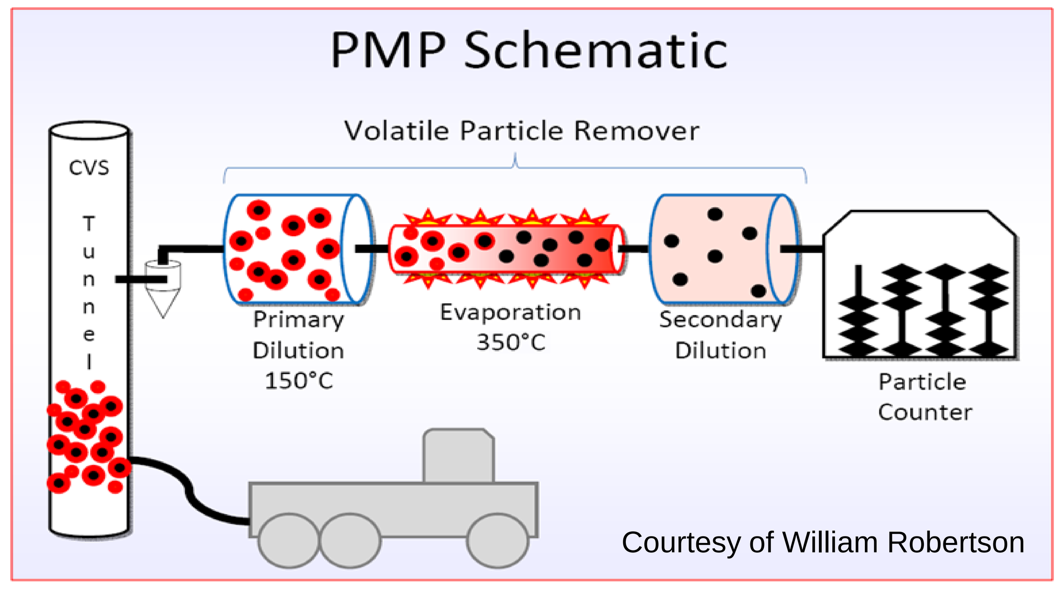
A Catalytic Stripper (CS) consists of two catalysts that convert the diluted exhaust gas components as well as volatile species on the surface of the particles. One catalyst is responsible for absorbing sulfur components and the other removes all volatile hydrocarbon components by oxidation [2]. The CS removes all particle precursors (volatile hydrocarbons and sulfur) and makes nucleation impossible downstream of the CS, whereas PMP system intends to suppress the nucleation by lowering the supersaturation ratio of the particle precursors. Ash particles and partially burned soot particles will make it past the CS, but re-renucleation will not occur with the CS.

Therefore, the CS is an ideal device to investigate the nature of particles under the PMP system. This study present laboratory and on-road in-use vehicle experiments of diesel particle penetration/formation under PMP protocol to assess its impact on the PMP measurement protocol using both PMP system and the Catalytic Stripper. The possible outcome of this study is suggestions to modification of current PMP method, which may result in suggestions to future implementation of the PMP method for in-use screening and rule making.

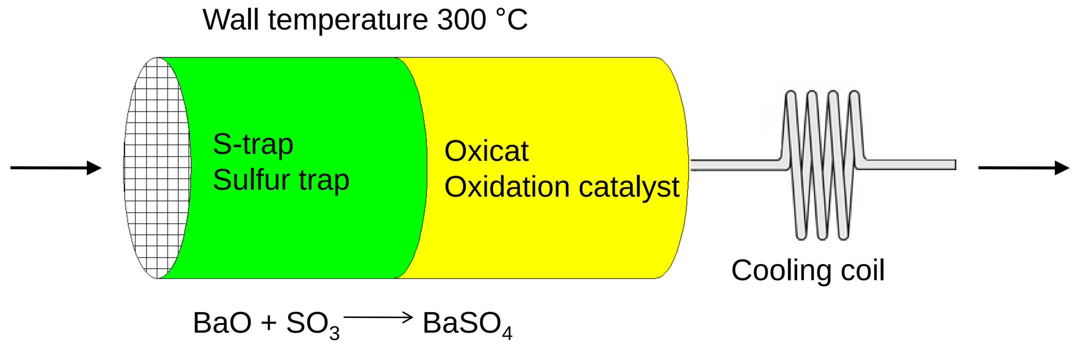
Objectives

- To evaluate the volatile species removal efficiency of European PMP system (a) using challenging volatile aerosol in the laboratory; (b) sampling from heavy-duty diesel vehicles operating at certain cycles.
- To investigate the nature of nucleation mode particles retained downstream of PMP system
- To compare PMP system with catalytic stripper sampling from a heavy-duty diesel vehicle under laboratory conditions on a chassis dynamometer and on-road conditions.

Schematics and experimental conditions

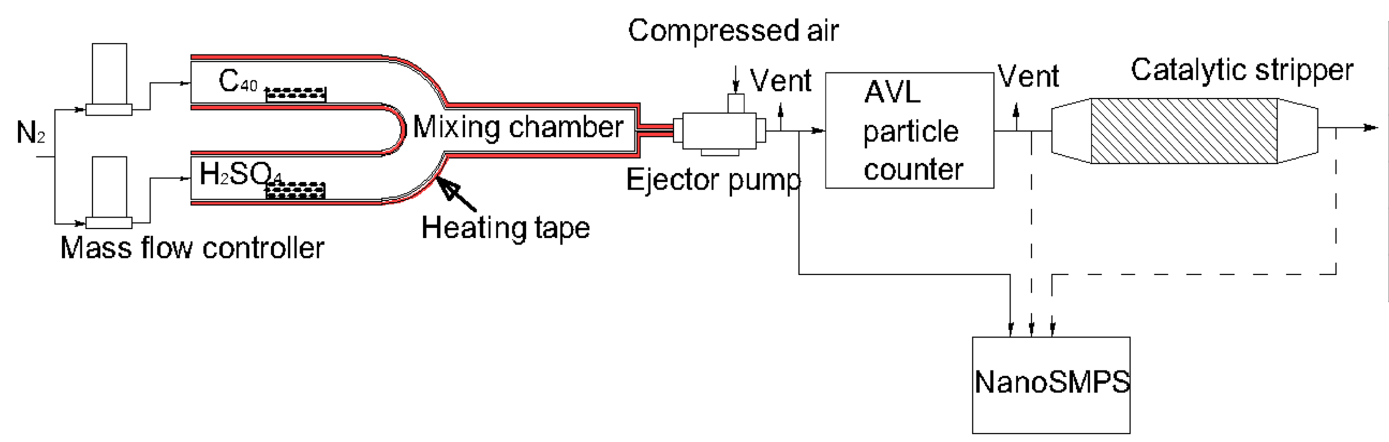


The PMP system used in this study was AVL particle counter (APC) [3]. It consists of a primary chopper diluter heated to 150 °C, a evaporation tube heated to 350 °C, a perforated tube as the secondary dilutor, and a TSI 3790 CPC with cut point of 23 nm.



The catalytic stripper (CS) consists of two traps, S-trap and Oxicat. S-trap removes SO3 by reaction show above and Oxicat has oxidation catalyst to help oxidize hydrocarbon compounds.

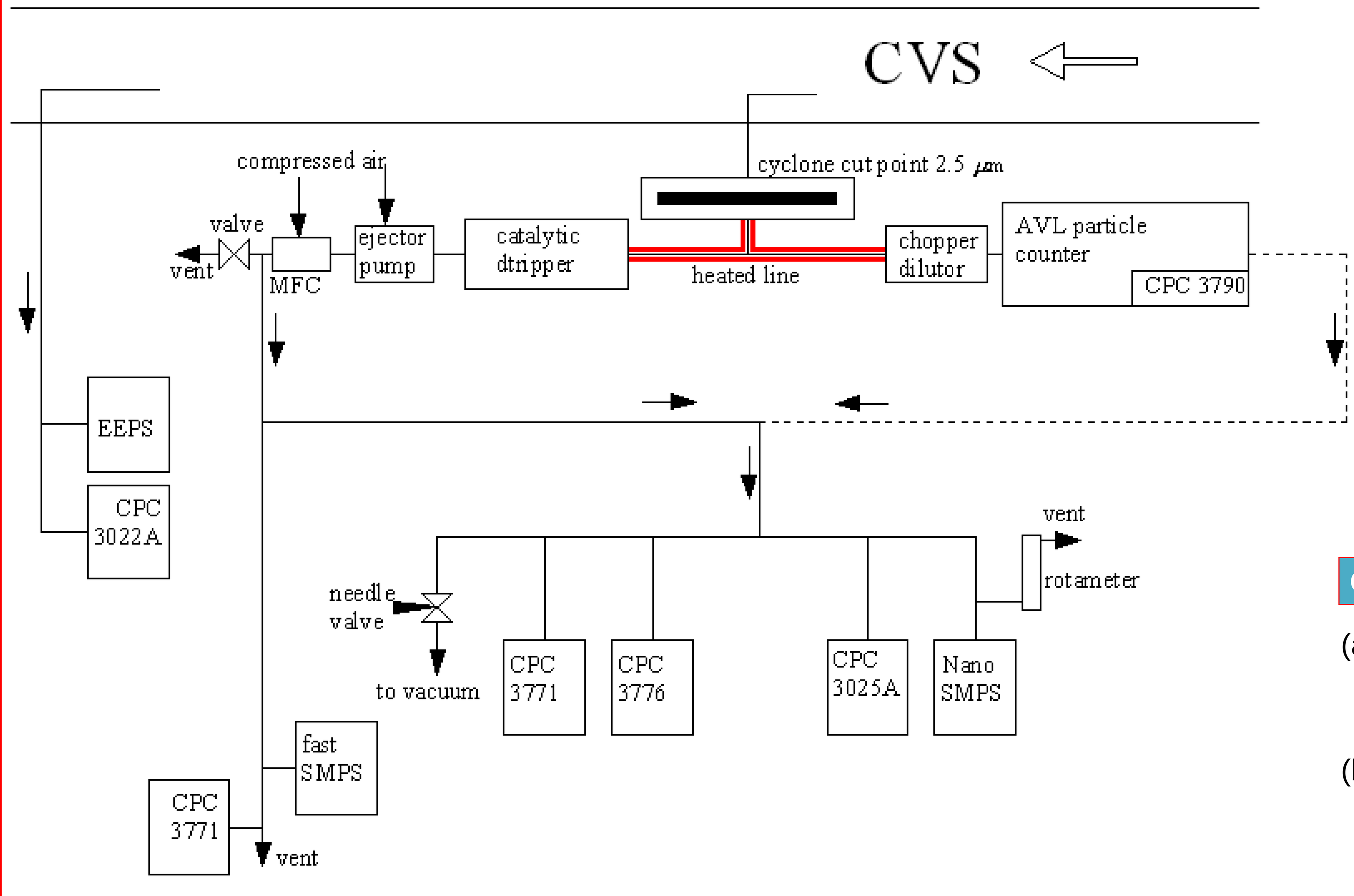
Schematic of lab test



Experimental condition of lab test

N2 flow rate	0.5 lpm
C40 temperature	160 °C
H2SO4 temperature	121 °C
Mixing chamber temperature	250 °C
APC primary dilution ratio	20
APC secondary dilution ratio	6

Flow Diagram of Chassis dynamometer test



Base	Chassis dynamometer
Vehicle	Freightliner class 8
Engine	Caterpillar C-15 (14.6L)
Fuel	ULSD
Lube oil	SAE 15W-40
DPF	JM CRT
Vehicle weight	65,000 lb
Cycles	(a) 25% load with constant speed of 50 mph (b) Following cycle a, 75% load with constant speed of 50 mph

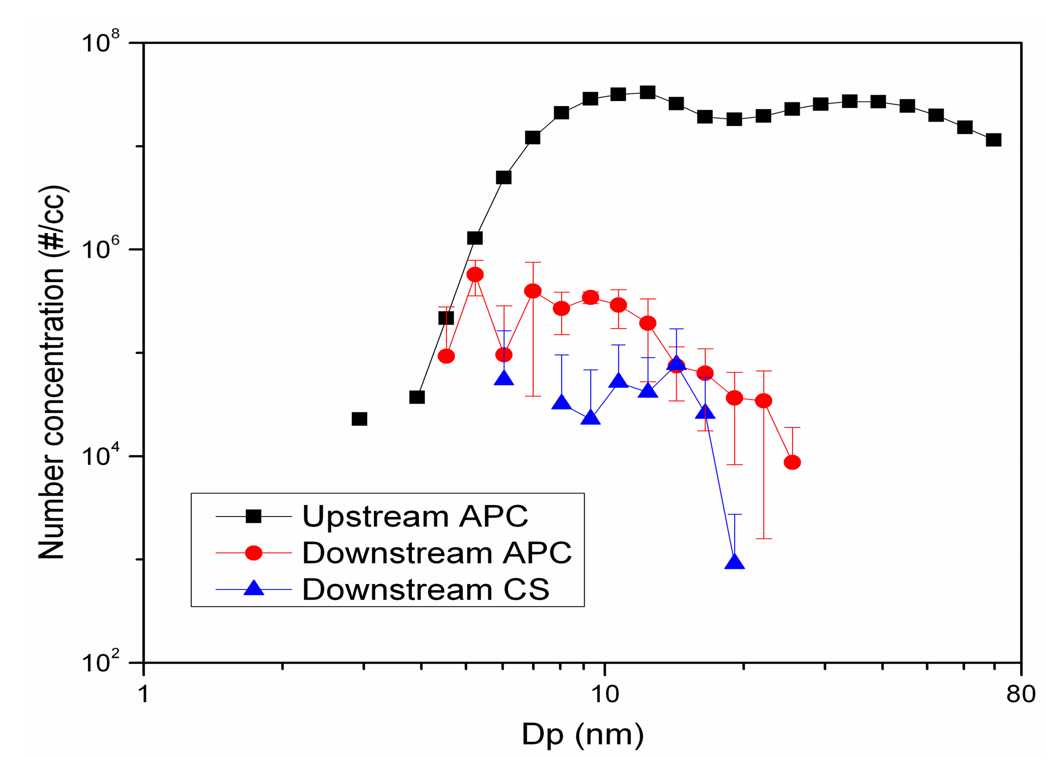
Characteristics of tested cycles

(a) 25% load: low exhaust temperature, storage of sulfate in the CRT, nucleation mode particle concentration low

(b) 75% load: high exhaust temperature, release of sulfate from the CRT, nucleation mode particle concentration high

Results

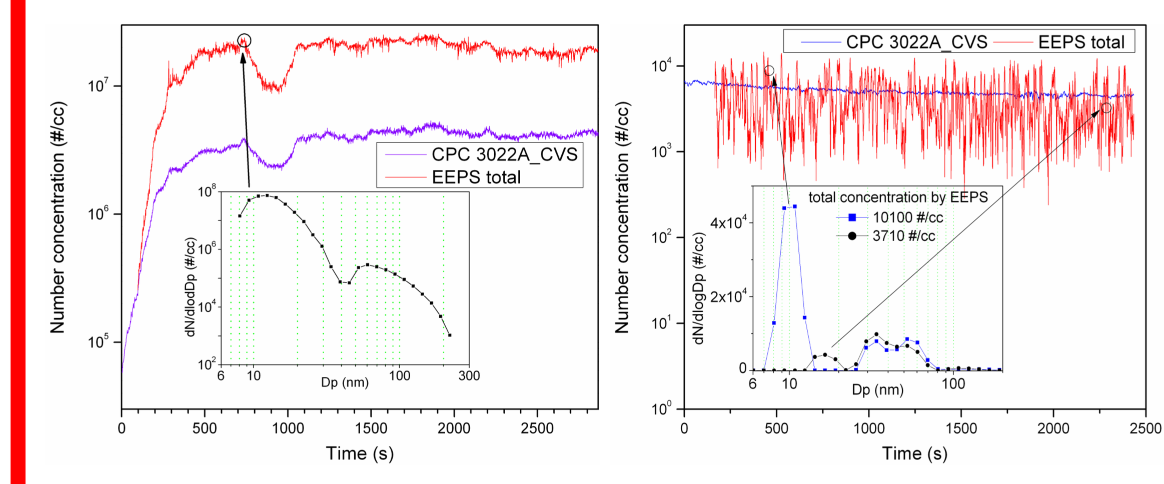
Size distributions of tetracontane (C40) and sulfuric acid (H2SO4) at upstream, downstream of AVL particle counter (APC), and downstream of catalytic stripper (CS).



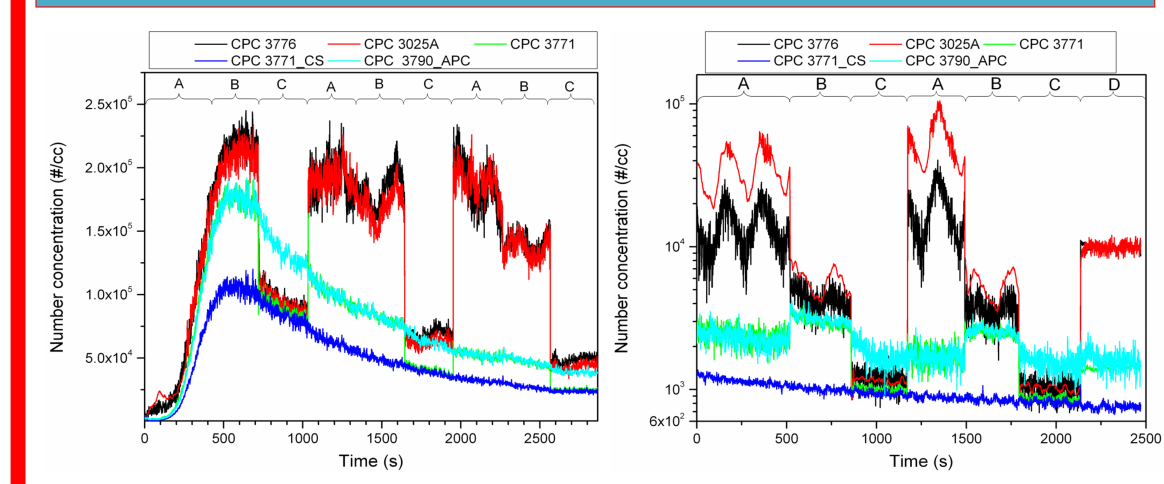
- At dilution ratio of 120, AVL Particle Counter was able to remove 99.9% C40 and H2SO4 particles. Small amount of nucleation mode particles survived in the evaporation tube.
- Catalytic stripper was connected downstream of AVL particle counter to investigate whether these particles were volatile or solid. A large fraction of these nucleation mode particles were detected at downstream of CS, suggesting these nucleation mode particles were solid.
- This result is consistent with previous study of thermal denuder and catalytic stripper [4]. The mechanism of nucleation mode solid particle formation downstream of AVL particle counter is unclear. More studies are needed.

75% load **25% load**

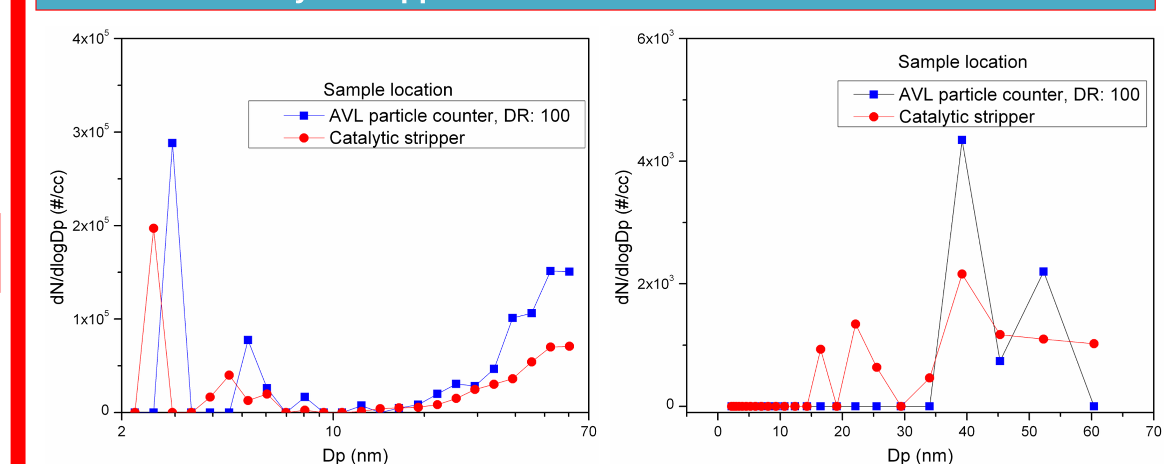
Real-time number concentrations measured by CPC 3022A and EEPS in the CVS; and typical size distributions measured by EEPS.



Real-time number concentrations measured by CPCs. Sampling location: A, AVL particle counter at dilution ratio of 500; B, AVL particle counter at dilution ratio of 100; C, catalytic stripper at dilution ratio of 17; D, directly from CVS.



Size distribution measured by nanoSMPS downstream of AVL particle counter and catalytic stripper.



- At 75% load, CPC 3022A measured about 2×10^6 #/cc real-time number concentration in the CVS, while EEPS measured about one order of magnitude higher. Size distribution showed that particles were primarily in the nucleation mode.
- At 25% load, real-time number concentration in the CVS were much lower than that of 75% load. Concentrations measured by CPC 3022A and EEPS agreed well.
- At 75% load, lower cut point CPCs (3025A and 3776) always measured higher number concentrations than those of higher cut point CPCs (3771 and 3790). The differences were more significant when sampling from APC.
- At 25% load, similar concentration differences between lower cut point CPCs and higher cut point CPCs were observed. However, 3025A had distinguishable higher concentration than 3776 when sampling from APC, dilution ratio of 500.
- When sampling from APC, at dilution of 500, concentrations measured by both 3025A and 3776 were higher than those of CVS, indicating APC was making particles.
- At 75% load, size distribution measured by nanoSMPS showed particles below 10 nm were present after both APC and CS systems, which was consistent with the CPC data. APC had higher concentration than CS.
- At 25% load, no particles below 10 nm were seen from nanoSMPS measurement, which was inconsistent with CPCs data. This may due to the low concentration and diffusion loss in the nanoSMPS system.

Conclusions

- Lab test with C40 and H2SO4 showed that APC was able to remove 99.9% volatile particles. However, nucleation mode "solid" particles were formed downstream of APC. Mechanism of formation is unclear.
- Lower cut point CPCs measured higher concentration than high cut point CPCs for both APC and CS. The differences of lower cut point CPCs and higher cut point CPCs were more significant for APC.
- At 25% load, constant speed of 50 mph, CPC 3025A measured higher concentration than CPC 3776 downstream of APC, indicating the possible presence of sub 3 nm particles.
- At 25% load, concentrations measured by lower cut point CPCs downstream of APC were higher than measured directly from CVS, suggesting new particle formation in the APC.
- Size distributions measured by nanoSMPS showed sub 10 nm solid particles were present downstream of both APC and CS at 75% load.

Acknowledgements

AVL for providing us the AVL particle counter.

Dr. Richard Frazee for his assistance and advice on operating AVL particle counter.

Mr. Donald Pacocha, for his contribution in setting up and executing this field project, the data collection and quality control.

Funding: California Air Resources Board

References

1. Johnson, K.C., et al., *Evaluation of the European PMP Methodologies during On-Road and Chassis Dynamometer Testing for DPF Equipped Heavy-Duty Diesel Vehicles.* Aerosol Science and Technology, 2009. **43**(10): p. 962 - 969.
2. Stenitzer, M. (2003). *Nano Particle Formation in the Exhaust of Internal Combustion Engines.* Diplom-Ingenieurs, Technischen Universität Wien, Fakultät für Maschinenbau (in English)
3. Giechaskiel, B., et al., *Calibration and accuracy of a particle number measurement system.* Measurement Science and Technology, 2010. **21**(4): p. 045102.
4. Swanson, J. and D. Kittelson, *Evaluation of thermal denuder and catalytic stripper methods for solid particle measurements.* Journal of Aerosol Science. **In Press**, DOI: 10.1016/j.jaerosci.2010.09.003.